ACID HYDROLYSIS OF POTATOES UNDER PRESSURE*

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Introduction

An important problem connected with the marketing of potatoes is the utilization of culls and surpluses. There are culls in every crop, and surpluses occur periodically because of fluctuations in yield and acreage. If whole potatoes could be hydrolyzed to give a concentrated self-preserving syrup, it would be possible to utilize these cull and surplus potatoes more efficiently. The syrup might be utilized as a source of fermentable carbohydrates or as feed. Potatoes could be stored and shipped more easily in this form than as whole potatoes.

Considerable information is available on the hydrolysis of pure starch (4), wood cellulose (2, 10), and agricultural residues (1) but not on the hydrolysis of potatoes. Hydrolysis of potatoes is complicated by the presence of proteins, pectins, and hemicelluloses. The pectins and pentosans would be expected to form furfural under the conditions of acid hydrolysis. Small amounts of hydroxymethyl furfural might be formed from the hexoses liberated. The Maillard reaction (5, 6) between amino acids and reducing sugars would likewise be expected.

To determine the feasibility of the acid hydrolysis of potatoes, experiments had been conducted at atmospheric pressure by other workers in this Laboratory. The potatoes were ground in a hammer mill, hydrolyzed in beakers in a steam bath at 90-95° C. to the point where the addition of iodine produced a wine-red color. The buffering effect of ground potatoes is considerable. For example, the pH values of ground potatoes and 1, 3, and 8 per cent of phosphoric acid were 3.2, 2.0, and 1.4, respectively. Corresponding values for water and phosphoric acid were much lower— 1.6, 1.3, and 1.0.

Table 1 shows that the starch in potatoes is much more difficult to hydrolyze than starch alone.

In other experiments, carried out at atmospheric pressure in a steam-jacketed kettle with good agitation, hydrolysis with 1 per cent hydrochloric acid (based on the weight of water in the potatoes) required 2 hours to reach the point at which iodine produced the wine-red color. After neutralization with sodium hydroxide, the solids content was 25 per cent. Sodium chloride constituted 5.7 per cent of the solids. Since the hydrolyzate contained only 16.5 per cent of soluble carbohydrates, fermentation took place

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TABLE 1.—*Time (hours) required to hydrolyze potatoes and starch at 90°—95°C.*

Acid	Hydrochloric Acid		Phosphoric Acid	
Per cent Acid[1]	Starch	Potatoes	Starch	Potatoes
1	1.9	30.4	7.1	>50
2	1.7	9.8	6.3	42
3	0.8	3.3	6.1	26.4
4	.7	2.7	5.3	14
6	.2	2.5	4.2	13.2
8	.1	2.1	2.1	12

[1] Based on the water content of the mixture.

rapidly. It had to be concentrated to more than 58 per cent total solids before it was self-preserving. At that point it contained about 39 per cent soluble carbohydrates and was a dark-brown, stiff, pasty mass with a bitter taste. A similar hydrolysis with 2 per cent hydrochloric acid required 30 minutes to reach the point of the wine-red reaction and had to be concentrated to 61 per cent solids (about 39 per cent soluble carbohydrates) to prevent fermentation. The 2 per cent acid offset the stiffness resulting from gelatinization of the starch, thus decreasing the power required for stirring. After neutralization, sodium chloride constituted 10.7 per cent of the solids. The stiff, pasty mass was difficult to dry. About 35 per cent solids (22 per cent soluble carbohydrates) was the maximum content that would permit the material to flow freely. This syrup required 0.1 per cent sodium benzoate to prevent fermentation.

It was assumed that hydrolysis under pressure would require less acid or a shorter time than the same process conducted at atmospheric pressure. The lower concentration of acid should result in a lower concentration of salt in the syrup after neutralization. Since the hydrolysis at atmospheric pressure was not satisfactory, we tested these assumptions by studying the hydrolysis under pressure.

EXPERIMENTAL METHODS

Hydrolyses: The washed potatoes were ground to pass through the coarse screen (2-mm. openings) of the Wiley mill. Sixteen pounds (7260 grams) of the ground potatoes were placed in a 2-gallon, glass-lined autoclave, and then the acid was added. The percentage of anhydrous acid was based on the weight of the whole potatoes. After the potatoes and acid were mixed, a sample was taken for a pH determination, and then the mixture was heated by steam in the jacket to the reaction temperature. In most cases, the kettle was closed when the contents started to boil, thus eliminat-

ing most of the air. About 1 hour was required to heat the contents to 130°C. Timing was begun when the mixture reached the desired temperature. The mixture was agitated continuously. At intervals samples were blown out through a sampling tube, and put in sterile pint fruit jars, which were immediately placed in the refrigerator and kept there until the contents were analyzed. Separate small samples were used for the pH determinations which were made with a Beckman Model G pH meter as soon as the sample had cooled. Iodine tests were made on the samples that might contain starch.

Analytical Methods: Moisture was determined by drying the materials to constant weight in a vacuum oven at 70°C. Sugar was determined by the standard A.O.A.C. method (7); the Munson-Walker method was used for determination of reducing power. The results are reported as per cent glucose. Total water-soluble carbohydrates were determined by a modified procedure for direct acid hydrolysis of starch (7). The sample was extracted by decantation through a filter with 300 mls. (50-ml. portions) of water at room temperature. The leaded and deleaded extract was heated for 2.5 hours under reflux on the steam bath with 30 mls. of hydrochloric acid (sp. gr. 1.125). The hydrolyzate was cooled, neutralized and treated as described for the direct acid hydrolysis of starch. The results are reported as per cent glucose. Starch was determined by the method of Steiner and Guthrie (9).

RESULTS

Table 2 shows the analyses of the various lots of potatoes. In table 3 are given the results of the hydrolysis experiments. The batch numbers in tables 2 and 3 show the order in which the analyses and determinations were made. Batches 1-6 represent one sample of potatoes grown in New Jersey, 7-12 represent a sample of Pennsylvania potatoes, 13-16 were from a second lot of Pennsylvania potatoes, and 17-22 were from a sample of Long Island potatoes. The potatoes were grown in the summer of 1948.

The solids in the first five batches (Tables 2 and 3) were probably low. These samples were dried in a forced-draft oven for 2 hours at 65° C. and then for 2 hours at 135° C. Under these conditions, considerable loss by decomposition took place. In batch 2, the whole lot was heated for 2 hours at 130° C. and then cooled by circulating cold water in the jacket. After neutralization to pH 5 with calcium oxide, the mixture was concentrated by heating at atmospheric pressure. In batch 4, 63 per cent of the starch was found in the sample taken when the mixture reached 130° C., 50 per cent in the sample removed after 1 hour, and none in samples taken after 2 hours. In batch 5 the corresponding starch values were 60, 38, and 25 per cent, respectively. Batch 21 contained 11 per cent starch when the temperature reached 130°C.

TABLE 2.—*Analyses of raw potatoes*
(*Moisture-free basis*)

Batch	Solids Per cent	Reducing Sugar Per cent	Total Sugar Per cent	Total Water-Soluble Carbohydrates Per cent	Starch Per cent	Calculated Hydrolyzable Carbohydrates[1] Per cent
1	19.3	0.3	1.5	1.4	65.7	74.4
6	20.0	<0.1	1.3	1.0	65.7	74.0
7	22.5	0.7	1.3	1.3	70.6	79.7
10	21.1	<0.1	1.3	1.3	74.1	83.5
14	22.9	0.4	....	1.3	69.8	78.9
18	24.4	....	....	2.2	71.2	81.3
22	26.9	0.9	....	3.2	68.4	79.2

[1] Calculated as glucose from the value for starch and water-soluble carbohydrates.

TABLE 3.—*Analyses of potato hydrolyzates*
(Moisture-free basis)

Batch	Condition of Hydrolysis					pH After hours at °C					Solids Per cent After hours at °C				
	Acid Kind	Acid Per cent	Temp., °C	Raw Potatoes	Potatoes with Acid	0	1	2	4	6	0	1	2	4	6
2	HCl	1.0	130	5.9	1.1	—	—	1.7	—	—	—	—	41.2	—	—
3	HCl	0.5	130	6.0	2.6	2.9	3.1	3.2	3.3	3.2	20.3	19.7	19.3	19.5	18.4
4	HCl	0.3	130	6.0	3.7	3.9	4.0	4.0	4.0	4.2	20.6	20.4	20.1	20.1	19.6
5	HCl	0.7	130	5.9	1.9	2.2	2.5	2.7	2.6	3.0	17.0	17.9	17.7	17.5	16.7
8	HCl	0.7	120	5.7	1.8	1.9	2.1	2.2	2.3	2.4	23.8	23.8	23.8	23.9	23.4
9	HCl	0.5	140	6.1	2.7	3.1	3.2	3.4	3.3	3.0	24.1	23.8	23.5	22.5	21.4
11	HCl	1.0	120	5.9	1.1	1.3	1.4	1.5	1.8	1.5	24.2	23.6	23.8	23.2	23.1
12	HCl	1.0	110	5.8	1.1	1.1	1.1	1.3	1.3	1.4	23.8	23.3	23.5	23.5	23.0
13	HCl	0.7	140	6.2	1.9	2.7	2.7	3.0	3.0	2.6	23.8	23.7	22.8	22.0	21.5
15	H$_2$SO$_4$	0.54	130	6.1	3.3	3.5	3.5	3.7	3.6	3.7	24.1	—	23.8	—	24.2
16	H$_2$SO$_4$	1.5	130	6.1	1.4	1.5	1.7	1.8	1.7	—	25.8	25.5	25.0	24.0	23.4
17	H$_2$SO$_4$	1.1	130	6.0	1.8	1.9	2.0	2.2	2.2	2.3	27.2	26.8	26.5	25.8	25.2
19	H$_3$PO$_4$	6.0	130	6.3	1.4	1.4	1.4	1.6	1.7	1.9	30.4	29.6	27.5	26.3	25.8
20	H$_3$PO$_4$	4.5	130	6.2	1.9	1.8	1.9	1.9	2.0	1.8	30.2	28.8	27.4	26.0	25.0
21	SO$_2$	2.0	130	6.3	2.7	3.5	3.3	3.2	2.8	2.5	28.0	27.5	27.8	27.9	27.5

TABLE 3.—*Analyses of potato hydrolyzates* (*Continued*)
(*Moisture-free basis*)

Batch	Acid Kind	Per cent	°C	Reducing Sugar Per cent — After hours at °C					Total Cold Water-Soluble Carbohydrates, Per cent — After hours at °C				
				0	1	2	4	6	0	1	2	4	6
2	HCl	1.0	130	----	20.1	74.4	39.7	47.0	62.3	85.4	74.4	79.4	76.4
3	HCl	0.5	130	6.4	3.4	28.2	7.5	8.7	13.7	36.5	85.4	69.5	78.0
4	HCl	0.3	130	2.1	58.1	4.6	76.3	79.4	99.9	92.2	57.5	81.4	78.6
5	HCl	0.7	130	28.1	42.3	73.3	61.7	64.8	77.9	78.1	89.9	71.7	69.5
8	HCl	0.7	120	16.4	21.4	54.5	43.2	52.2	77.8	77.2	77.0	65.3	58.1
9	HCl	0.5	140	10.6	71.3	31.2	73.9	73.1	78.6	79.0	72.7	77.3	75.0
11	HCl	1.0	120	51.1	54.9	72.5	68.6	71.5	77.1	76.0	77.0	75.6	75.9
12	HCl	1.0	110	24.2	60.5	63.2	66.0	64.0	77.8	74.4	76.3	65.9	64.2
13	HCl	0.7	140	40.6	----	65.3	----	11.5	16.0	----	71.7	----	73.9
15	H₂SO₄	0.54	130	2.1	42.7	5.1	61.7	61.7	75.9	75.2	53.4	62.3	57.1
16	H₂SO₄	1.5	130	13.3	25.2	56.4	48.8	55.9	59.8	78.8	70.1	71.6	66.8
17	H₂SO₄	1.1	130	7.3	54.3	35.8	50.1	43.0	66.6	60.5	77.6	43.1	35.3
19	H₃PO₄	6.0	130	25.6	49.5	56.5	56.1	48.8	69.9	65.5	54.5	46.6	40.0
20	H₃PO₄	4.5	130	14.4	----	57.2	----	----	----	----	58.2	----	----
21	SO₂	2.0	130	6.0	11.5	18.6	33.0	46.9	46.8	76.2	76.8	69.8	64.3

DISCUSSION OF RESULTS

Figure 1 illustrates the changes which took place during the hydrolysis of batch 3. The pH change on addition of acid is shown at the left of the vertical axis. The pH gradually increased as hydrolysis proceeded, perhaps because of formation of salt with the amino acids freed. The starch had nearly disappeared by the time the mixture reached the temperature of the experiment and nearly all of it had been converted to water-soluble forms. The value for water-soluble carbohydrates reached a maximum value and then began to decrease as heating progressed. This loss in reducing power indicated decomposition of the sugars. At the same time, the pressure in the autoclave continued to increase (at constant temperature). The gas in the autoclave responsible for the increase of pressure contained carbon dioxide. When decomposition was considerable, the pressure in the kettle rose to two or three times that of saturated steam at the temperature used. The hydrolysis to glucose was not complete after 6 hours. If the hydrolysis were complete, the curves for sugar and water-soluble carbohydrates would meet and then coincide. It is important to note, however, that the hydrolysis brought about complete conversion of the starch to a water soluble form after 1 hour. For some uses, this might be a good stopping point, avoiding the unnecessary decomposition of carbohydrate material.
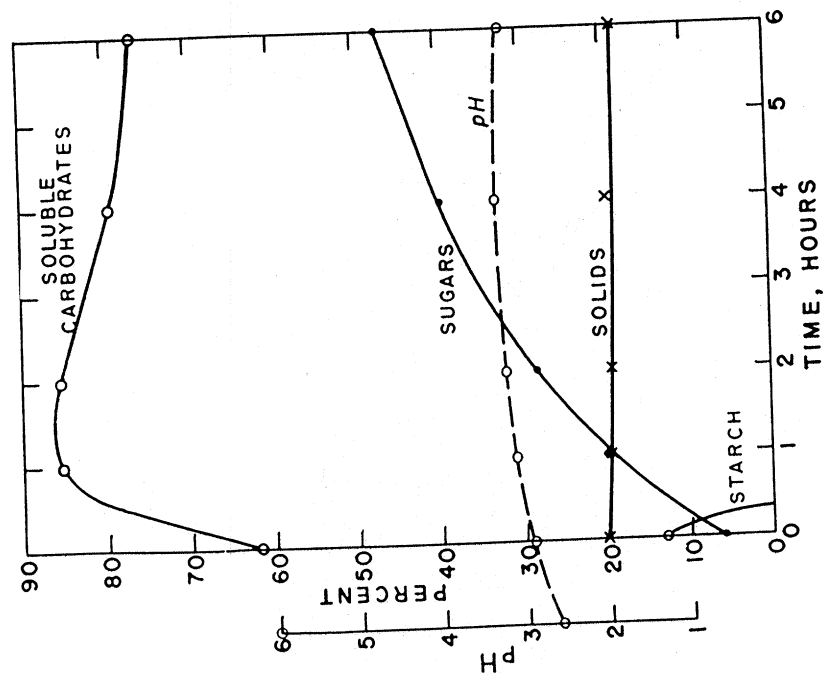

Fig.1, Hydrolysis with 0.5% HCl at 130° C. (Batch 3)

The results represented by figure 1 are more or less typical. Figure 2 shows the results when hydrolysis was practically complete in 6 hours (batch 12). The maximum gauge pressure in this case was 12 pounds, and little decomposition occurred. In figure 3 is illustrated another example of practically complete hydrolysis in 6 hours. Here, however, with a lower concentration of acid and a higher temperature than in batch 12 (Figure 2), the loss in reducing power was more than 25 per cent in 6 hours. That this loss was caused mainly by the increase in temperature was confirmed by the following experiment: A batch of potatoes was hydrolyzed under the conditions used for batch 12, illustrated in Figure 2. After 6 hours heating at 110°C. the mixture was cooled and neutralized to pH 5 with sodium hydroxide, and then heated at 140°C. After 6 hours' further heating, the reducing power had dropped to less than one-half the value shown in figure 2.
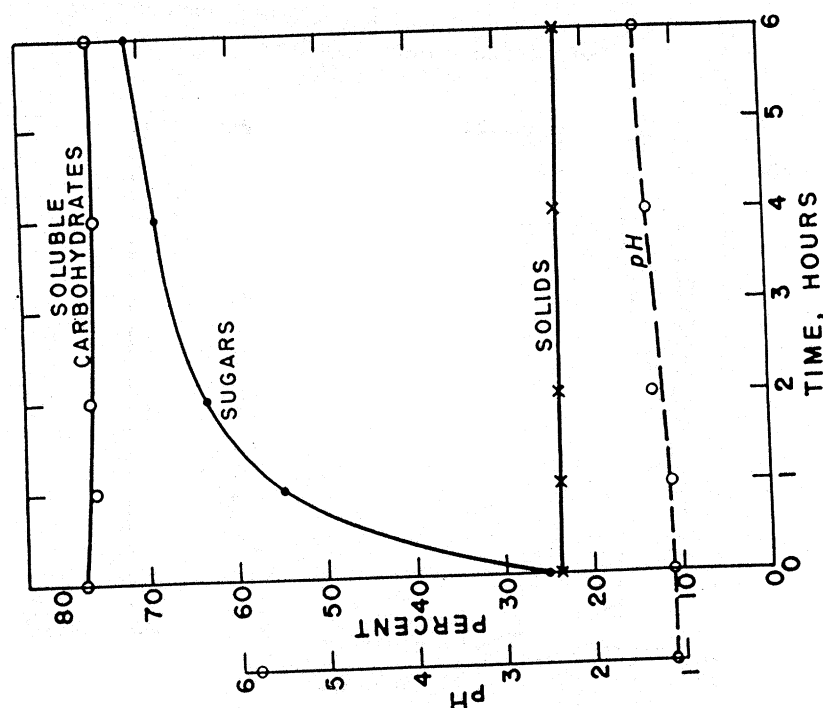

Fig. 2. Hydrolysis with 1.0 % HCl at 110°C. (Batch 12)

With acids other than hydrochloric, the results were similar except that the loss in reducing power was greater. The results with sulfuric acid were not far different from those obtained with hydrochloric acid, but larger amounts of sulfuric acid were needed to achieve the same results. Still larger amounts of phosphoric acid were required. Figure 4 shows the results of one run with phosphoric acid. As compared with results of hydrolysis with corresponding amounts of hydrogen chloride, loss in reducing power was greater, loss in solids occurred, the pH remained more constant, and the curves representing sugar and water-soluble carbohydrates cross. In hydrolyses with hydrogen chloride, these curves approached each other or even coincided, but they do not cross in any case, nor would they be expected to cross.

The significance of the crossing of the curves in the case of phosphoric acid is not clear. Control experiments were run in which glucose solutions with and without sodium phosphate were analyzed according to these procedures. The same results were obtained with both solutions, indicating that the crossing of the curves was not due to errors in analysis caused by the presence of phosphate or phosphoric acid.
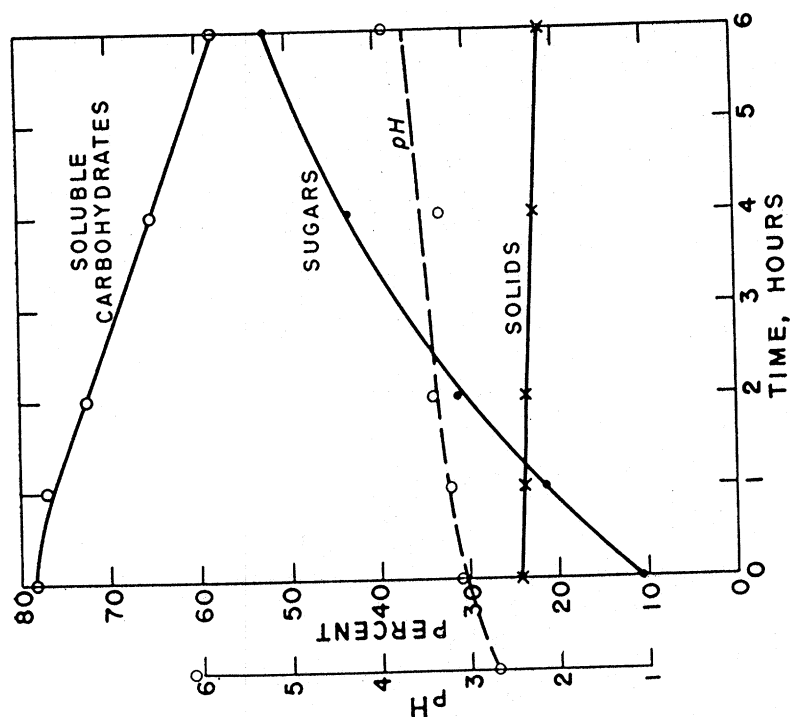

Fig.3. Hydrolysis with 0.5% HCl at 140°C. (Batch 9)

Sulfur dioxide was tried with the results shown in figure 5. In contrast with results with the other acids, the pH value decreased with progress of heating. Perhaps the sulfurous acid was converted to a stronger, possibly non-volatile acid. The solids content remained constant.

In figure 6 are summarized the effects of the various acids on the rate of formation and decomposition of reducing sugar. In all the hydrochloric acid experiments, there was a continuous increase in the reducing value. As previously mentioned, the values for 0.7 per cent hydrochloric acid were somewhat high because of errors in determining solids. With 1.5 per cent sulfuric acid, the curve flattened out, and with phosphoric acid the reducing value reached a maximum and then decreased, indicating decomposition. In figure 7, in which total water soluble carbohydrate content is plotted against time, the tendency of the acids to cause loss in reducing power is shown more strikingly. Here again the rate of decrease in reducing power was least with hydrochloric acid. In order of increasing effect the catalysts were: hydrochloric acid, sulfuric acid, sulfur dioxide, and phosphoric acid. In fact, with the higher concentrations of sulfuric and phosphoric acids,
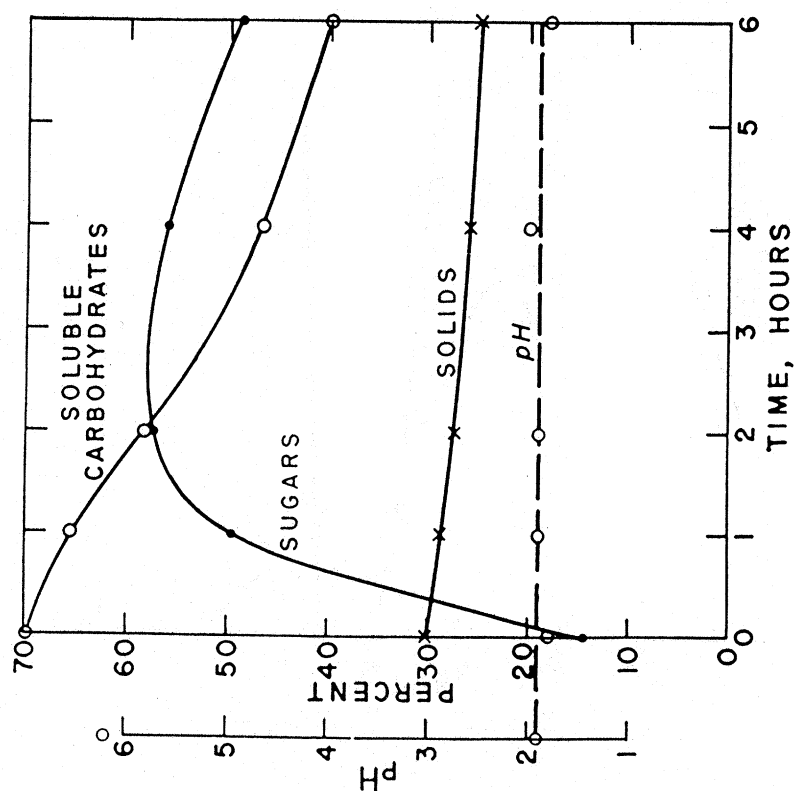

Fig. 4. Hydrolysis with 4.5 % H_3PO_4 at 130° C. (Batch 20)

the yields were lower, although the maximum was reached sooner. It may be noted that 0.7 per cent hydrochloric acid, 1.1 per cent sulfuric acid, and 4.5 per cent phosphoric acid produced mixtures having a pH of approximately 1.9. The curves for the three acids, however, are quite different.

In a number of cases a plot of the logarithm of the percentage residual potential reducing sugar (the difference between sugar and total water soluble carbohydrates in per cent of the latter) against time gave straight lines, indicating that the rate of hydrolysis followed a first-order reaction; that is, the rate depended only on the concentration of the unhydrolyzed carbohydrate if the acid concentration and temperature were constant (8, 3). In other cases, such lines were somewhat curved. To obtain a better idea of the relative rates, the reaction constants were calculated from the slopes of the lines. No great accuracy is claimed for the constants; they are given only to indicate the relative rates of reaction. The constants (time in hours, natural logarithms) are listed in table 4. When only one value is given, the value was constant throughout the range studied; otherwise a range of values is given. With hydrogen chloride and a temperature of approximately 130°C., an increase of 20° about doubled the rate of reaction.
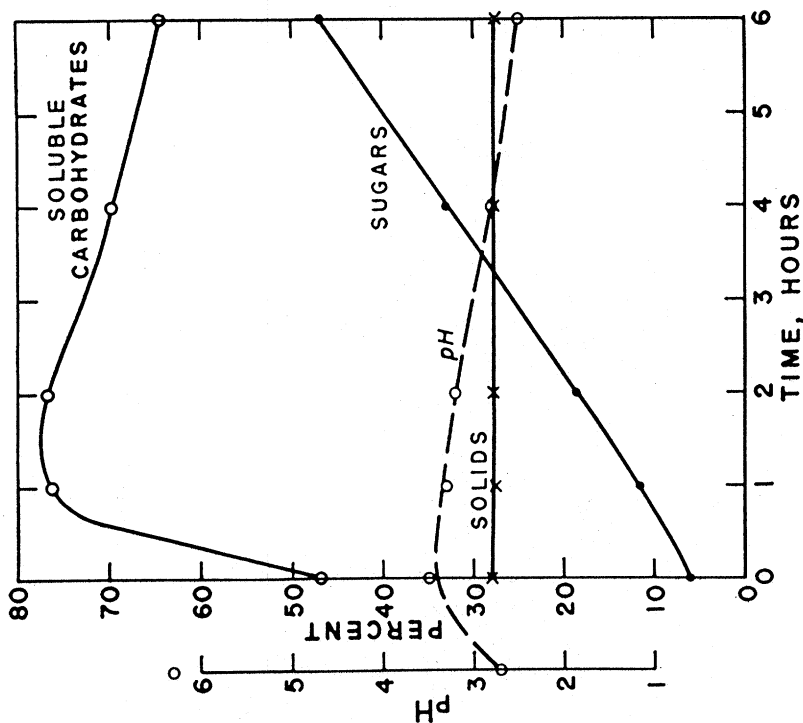

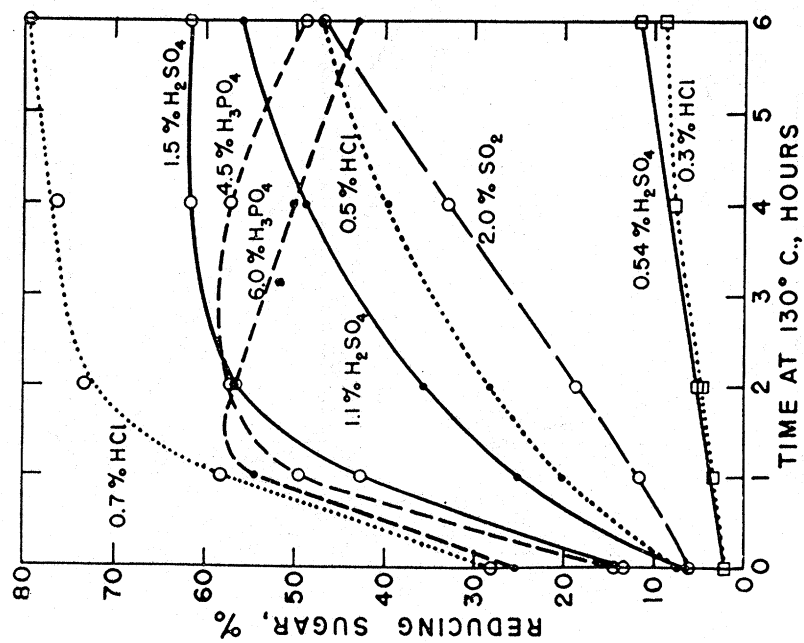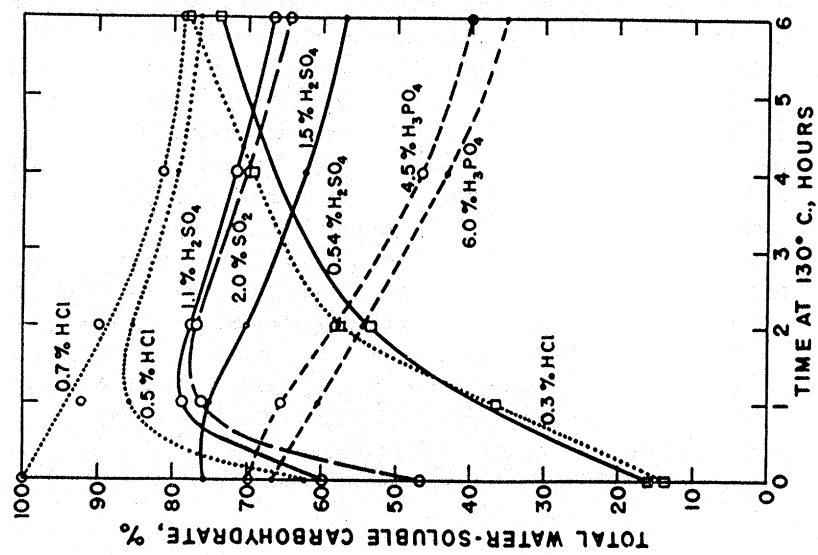Fig.5. Hydrolysis with 2.0% SO_2 at 130°C. (Batch 21)

Fig.7 Effect of acid on total water-soluble carbohydrate yield.

Fig. 6 Effect of acid on reducing sugar yield.

TABLE 4.—*Relative reaction rates.*

Batch	Acid		Temperature-°C.	Rate Constant hr^{-1}
	Kind	Per cent		
19	H$_3$PO$_4$	6.0	130	1.8—?
20	H$_3$PO$_4$	4.5	130	1.2—0.36?
11	HCl	1.0	120	1.3—0.21 ; 0.44 av.
13	HCl	0.7	140	0.86
12	HCl	1.0	110	0.90—0.23 ; 0.41 av.
5	HCl	0.7	130	0.62
16	H$_2$SO$_4$	1.5	130	0.54
8	HCl	0.7	120	0.41
17	H$_2$SO$_4$	1.1	130	0.25
21	SO$_2$	2.0	130	0.025—0.33 ; 0.20 av.
9	HCl	0.5	140	0.24
3	HCl	0.5	130	0.14
15	H$_2$SO$_4$	0.54	130	0.026
4	HCl	0.3	130	0.014

Increasing the concentration from 0.3 to 0.5 per cent hydrogen chloride increased the rate about tenfold. An increase from 0.5 to 0.7 per cent tripled the rate, and an increase from 0.7 to 1.0 per cent increased the rate two to three times. Approximately the same rate was obtained with 1.5 per cent sulfuric acid as with 0.7 per cent hydrogen chloride, and this was nearly doubled with 4.5 per cent phosphoric acid.

Hydrochloric acid is used as a catalyst in the commercial acid hydrolysis of starch (4). Work on the hydrolysis of wood cellulose (3) and that reported here indicate that in both cases hydrochloric acid is more efficient than sulfuric acid. In large scale tests on both wood (2) and agricultural residues (1), however, sulfuric acid has been used, probably because it is the cheapest acid. The relative prices/ (per hundred pounds) on a water-free basis are: sulfuric acid, $0.89; sulfur dioxide ,$4.50; hydrochloric (muriatic) acid, $5.92, and phosphoric acid, $6.00. Sulfur dioxide would be rather expensive, since a large quantity would be required, but part of it at least might be removed by volatilization, thereby decreasing the amount of salt retained in the final product after neutralization.

The products of the hydrolyses described here were dark and bitter. The material was difficult to concentrate beyond 40-45 per cent solids because it became a stiff, sticky paste. At this concentration, it was not self-preserving because it contained only about 30-35 per cent of sugars. Concentrated samples molded in the laboratory.

/The lowest prices calculated from the prices listed in the Oil, Paint, and Drug Reporter for November 28, 1949.

Conclusion

The acid hydrolysis of potatoes does not appear promising as a method of processing cull and surplus potatoes for storage or transportation. Elevated pressures do not seem to have much advantage, although they produce results in a shorter time or with less acid. To avoid decomposition, high acid concentrations would be required, and the resulting syrups would be difficult to concentrate. The statement, "In order to be suitable for commercial use, the agent promoting hydrolysis must give a high rate of hydrolysis as compared with the rate of sugar decomposition" (3) applies with the same force to the hydrolysis of potatoes as to the hydrolysis of wood cellulose. The rate of decomposition of potato hydrolyzates seems to increase more rapidly with temperature than the rate of hydrolysis, and the ratio is more favorable for wood cellulose than for potatoes. This method of hydrolysis is more promising when the hydrolyzates are to be used as fermentation substrates and when it is not necessary to hydrolyze the starch completely to glucose. Relatively high acid concentrations and close control would be required to keep decomposition to a minimum. Under properly controlled conditions, the results might well be satisfactory. Use of the material as a fermentation substrate would not require the expensive concentration step.

Acknowledgements

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